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(54) SOAP

(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain, of Port Sunlight, Birkenhead, Cheshire, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to soap and in particular to soap compositions for personal washing, commonly called toilet soaps. Such soap compositions, which may contain conventional additives including perfumes, fillers, colourants, germicides, preservatives and free fatty acids, commonly take the form of bars or tablets but may also be used in powdered or liquid form.

The term "soap" as used herein refers to water-soluble salts of higher fatty acids, particularly the alkali metal salts, for example the sodium salts, thereof. Conventionally, the fatty acids used in soaps have chain lengths comprising from 8 to 20 carbon atoms, usually from 12 to 18 carbon atoms. Although the fatty acids are in salt form in soap compositions, apart from any minor free fatty acid content therein, where convenient the soaps of the invention are described in terms of their fatty acid content for ease of description.

Conventional toilet soaps are commonly made by saponification of a mixture of tallow and nut oils, the latter including particularly palm kernel and coconut oils. The lathering properties of nut oil soaps are generally much better than those of tallow soaps, but it is not the general practice to make a toilet soap exclusively from nut oil fatty acids as such soaps are thought sometimes to cause skin irritation. Moreover, nut oils are usually much more expensive than tallow, so that the use for soap production of a high proportion of the latter is economically desirable. But soaps formed exclusively from tallow fatty acids tend to have unacceptably poor lathering properties for personal washing.

It is an object of the present invention to provide a soap with good lathering properties made from tallow and synthetic fatty acids.

According to the present invention a soap is derived from tallow fatty acids and synthetic fatty acids, which synthetic fatty acids include from 5 to 30 per cent by weight of C_{11}—C_{15} branched chain fatty acids, the percentages being based on the total amount of fatty acids.

The present invention is based on the surprising discovery that the presence in the soap of a proportion within the range specified of the branched-chain fatty acids considerably improves its lathering properties. The use of too low or too high a proportion of the branched-chain fatty acids has been found to give less satisfactory lathering properties.

It has been proposed hitherto to incorporate soaps of synthetic fatty acids into toilet bars. Specifically, it has been suggested to add to a germicidal soap bar a sodium or potassium salt of α-methyl tetradecanoic acid as a potentiator for the germicide. However, the surprising benefit of using specific amounts of branched chain C_{11}—C_{15} synthetic fatty acids in the formation of soap bars has not been appreciated hitherto. We disclaim the use of solely α-methyl tetradecanoic acid as the branched chain fatty acids in the soap according to the present invention.

It is generally preferable, for economic reasons, to prepare the soaps of the invention from a major proportion, that is at least 50 per cent by weight, of tallow fatty acids. The term "tallow fatty acids" is used in this specification to refer to fatty acids of the type which can be produced from tallow-class fats, for example beef tallow, mutton tallow, lard, palm oil and some vegetable butters. The fatty acids, which can be derived by saponification of tallow-class fats followed by acidification of the resultant soaps, contain no substantial amounts of fatty acids having carbon chain lengths of equal to or less than 12 carbon atoms, at least 35 per cent by weight of oleic acid and not more than 60 per cent by weight

of unsaturated fatty acids. However, such fatty acids may be hardened or purified by distillation or otherwise prior to their use in the soaps of the invention, if desired. Further, the fatty acids may be derived from tallow-class fats after subjecting the latter to hardening processes. Thus, the tallow fatty acids used in the soaps of the present invention need not contain 35 per cent or more by weight of oleic acid as mentioned above, but do contain no substantial amounts of fatty acids having carbon chain lengths equal to or less than 12 carbon atoms, and generally the amounts of higher fatty acids are within the ranges:

	%
C_{14}	0—10
C_{16}	20—45
C_{18}	45—80

The proportion of the branched-chain fatty acids incorporated in the soap of the invention is preferably at least 10 per cent by weight, on the total amount of fatty acids in the soap. Generally, optimum lathering properties are found in soaps according to the invention comprising about 20 per cent by weight of the branched-chain fatty acids.

Branched-chain fatty acids suitable for use in the soaps of the present invention may be prepared for example, by oxidation of fatty alcohols produced by an 'Oxo' process, in which olefinic hydrocarbons of suitable chain length are catalytically reacted with carbon monoxide and hydrogen. The product of this process is a mixture of branched-chain and linear alcohols, the proportions and types of which are variable according to the conditions of reaction and the catalyst used, as well as the nature of the starting material. The fatty acids produced by oxidation of the 'Oxo' alcohols generally contain a proportion of branched-chain fatty acids within the range of from 20 to 80 per cent by weight.

Alternative suitable branched-chain fatty acids may be prepared by a Koch-type reaction from a linear or branched-olefin, which latter may be prepared, for example, by dimerisation or co-dimerisation of short-chain olefins. The products of this process are branched-chain fatty acids of the type termed "neo"-fatty acids, which contain quaternary α-carbon atoms. In the Koch-type reaction, the olefin is catalytically reacted with carbon monoxide and water.

The proportion of branched-chain fatty acids in the sample of synthetic fatty acids used in the production of a soap according to the invention affects the amount of the synthetic fatty acids which must be admixed with tallow fatty acids to give a proportion of branched-chain fatty acids within the range required. Thus, for example, the amount of a sample of synthetic fatty acids containing 50 per cent of branched-chain fatty acids which may be admixed with tallow fatty acids is from 10 to 60 per cent by weight, in order to provide in the soap produced therefrom salts of from 5 to 30 per cent of branched-chain fatty acids. As it is generally desirable to use a high proportion of tallow fatty acids in the production of the soaps, it is preferable to use types of synthetic fatty acids containing high proportions of branched-chain fatty acids, particularly synthetic fatty acids containing at least 40 per cent by weight of branched-chain fatty acids. Using a synthetic fatty acid containing at least 40 per cent by weight of branched-chain fatty acids makes it possible to form a soap from a major proportion of tallow fatty acids and a proportion of synthetic fatty acids such that the soap comprises about 20 per cent by weight of branched-chain fatty acids. Synthetic fatty acids comprising substantially wholly branched-chain fatty acids are preferably used when it is desired to make soaps comprising higher proportions of tallow fatty acids.

Suitable types of branched-chain synthetic fatty acids, or branched-chain fatty alcohols which can be oxidised to such acids, can be obtained commercially. The utility of the acids in the soaps according to the present invention depends to a very considerable extent on their price in comparison with the available nut oils. It is envisaged that the price of the synthetic fatty acids will decrease with their greater production and use, so making their use in accordance with the invention of increasing economic benefit, whilst allowing the use of nut oils for consumption in edible products. Moreover, the use of the synthetic fatty acids in the soaps of the invention leads in many cases to their improved lathering properties in comparison with soaps made from natural fatty acids only.

The soap according to the invention may be made by neutralisation of a mixture of tallow and synthetic fatty acids of which a proportion within the range stated are branched-chain fatty acids. Alternatively, the soap may be made by admixture of two or more different soaps, at least one of which contains branched-chain fatty acids, in proportions such that the blended soap contains an amount of branched-chain fatty acids within the range stated.

In addition to the essential tallow and synthetic branched-chain fatty acids, soaps according to the invention may incorporate amounts of other synthetic fatty acids, preferably C_{11}—C_{15} fatty acids. The presence of such other synthetic fatty acids cannot be avoided if the type of synthetic fatty acids admixed with the tallow fatty acids does not consist entirely of branched-chain fatty acids. Additionally, the soap may incorporate amounts of fatty acids of natural origin other than tallow, for example nut oil soaps, but

this is generally undesirable on economic grounds. It is preferable not to incorporate in the soaps of the invention significant proportions of either linear or branched-chain fatty acids having carbon chain lengths of 16 or more, apart from the tallow fatty acids, as their presence generally has a deleterious effect on the lathering properties of the soaps.

Soaps according to the invention are further described by way of the Examples below. In all of the Examples parts and percentages are by weight except where otherwise indicated.

EXAMPLES 1 TO 4

A series of soaps were made by neutralisation of various mixtures of tallow fatty acids and of a sample of synthetic fatty acids containing 64% of branched-chain fatty acids, and also from the tallow and synthetic fatty acids alone. The soaps thus produced contained nominal proportions of branched-chain fatty acids varying from 0 to 64% on the total fatty acids present. Neutralisation was accomplished in each case by adding a quantity of the fatty acids to the theoretical quantity of a boiling 50% aqueous alcoholic solution of sodium hydroxide. The resultant soap solution was maintained slightly alkaline to phenolphthalein and refluxed for 30 minutes. The water and the alcohol were then evaporated to leave a soap which was ground to a fine powder. The resultant dried soap contained less than .02% of free alkali (calculated at Na_2O) and no free acid.

The sample of synthetic fatty acids used contained about 31% of C_{11} carboxylic acids, about 51% of C_{13} carboxylic acids and about 18% of C_{15} carboxylic acids; of the total fatty acids about 36% were linear fatty acids, about 38% had α-methyl substituent groups, about 7% had α-ethyl substituent groups and the remainder were otherwise more highly branched.

The lathering properties of each of four soaps according to the invention and of four comparative soaps, all made as described above, were determined by making 5% by weight/volume aqueous solutions of the soaps and then measuring the volumes of lathers produced at 30°C under standard conditions. The results of the lathering tests are given in Table 1 below with details of the proportions of tallow and synthetic fatty acids in the soaps tested.

TABLE 1

Soap Description	Branched-chain fatty acids (%)	Lather Volume (Average mls)
Comparative soap (All tallow fatty acids)	0	85
Example 1	5	110
Example 2	10	150
Example 3	20	200
Example 4	30	130
Comparative Soap (Low tallow content)	40	100
Comparative soap (Low tallow content)	50	50
Comparative soap (All synthetic fatty acids)	64	0

These results demonstrate beneficial synergistic lathering properties for the soaps prepared from the mixtures of tallow and synthetic fatty acids giving proportions of branched-chain fatty acids on the total fatty acid content within the range of from 5 to 30%, with the optimum lathering properties being attained at about 20% branched-chain fatty acid content. The soaps prepared from the tallow fatty acids alone, from the synthetic fatt acids alone, or from too high a proportion of the synthetic fatty acids in mixtures with the tallow fatty acids had distinctly inferior lathering properties.

EXAMPLE 5

Two soaps were prepared separately from a sample of tallow fatty acids and synthetic fatty acids and then admixed in appropriate

proportions, instead of admixing the fatty acids prior to neutralisation as in Examples 1 to 4. The sample of synthetic fatty acids was very similar to that used in Examples 1 to 4, and contained about 64 per cent of branched-chain fatty acids.

The lathering properties of the soap were then determined and may be compared with those for soaps made from tallow fatty acids and the synthetic fatty acids alone. The results obtained are set out in Table 2 below.

TABLE 2

Soap Description	Branched-chain fatty acids (%)	Lather Produced (Average — mls)
Tallow soap	0	130
Example 5 (2 parts tallow soap to 1 part synthetic soap)	21	225
Comparative soap (1 part tallow soap to 2 parts synthetic soap)	43	125
Synthetic Soap	64	0

These results demonstrate the very much better lathering properties of the soap of Example 5 which contains soaps of a proportion of branched-chain fatty acids within the range according to the invention. Both the tallow soap alone, the comparative (low tallow) soap and the synthetic soap alone have inferior lathering properties which are unsatisfactory for personal washing purposes.

For the purposes of further comparison, in order to demonstrate the necessity for the presence of a proportion of branched-chain rather than linear synthetic fatty acids, a further soap was prepared from a sample of linear C_{11}—C_{15} fatty acids containing approximately equal proportions of each of the C_{11}, C_{12}, C_{13}, C_{14} and C_{15} saturated fatty acids. Mixtures of this soap with soap from tallow fatty acids in the ratios of 1:2 and 2:1 were prepared and their lathering properties determined with the results given in Table 3 below:—

TABLE 3

Soap Description	Lather Produced (Average results in mls)
Comparative soap (2 parts tallow soap to 1 part synthetic (linear) soap)	125
Comparative soap (1 part tallow soap to 2 parts synthetic linear soap)	130
Synthetic (linear) soap	130

These results may be compared with those in Table 2 and demonstrate a lack of synergistic lathering in the absence of the branched-chain fatty acids.

EXAMPLE 6

An 80:20 mixture of tallow fatty acids and a sample of predominantly C_{15}, randomly-branched synthetic fatty acids, prepared by a Koch-type reaction from a branched olefinic hydrocarbon feed-stock, was melted and heated to 70°C in a kneading machine. A caustic soda solution (30% NaOH) was added slowly to the mixed fatty acids until the soap was slightly alkaline to phenolphthalein. The soap mass produced was chilled and then air dried at 90°C after which the dried soap was milled and plodded to form soap tablets.

The lathering properties of the soap tablets were determined at both 20°C and 40°C by a procedure in which the tablets were wetted and rubbed between the hands in a standard manner. The results of the lathering tests are given below in Table 4 with the lathering test results for similar soap tablets prepared for purposes of comparison from a mixture of tallow fatty acids and palm kernel oil fatty acids in the ratio of 80:20.

TABLE 4

Soap Description	Lather Volume (Average results in mls) 20°C	40°C
Example 6	366	303
Comparative soap	338	288

These results show that the use of the wholly branched-chain synthetic fatty acids instead of palm kernel oil fatty acids gave a small improvement in lathering properties. However, when soap tablets were made by a similar procedure but with an increased synthetic fatty acid content of 50%, to give 50% branched-chain fatty acids in the soap, the lathering properties of the tablets were found to be decreased very much and were then inferior to a soap made for comparative purposes from tallow fatty acids and palm kernel oil fatty acids in the ratio of 50:50.

EXAMPLE 7

Two types of soap tablet were prepared by admixture of tallow fatty acids and a sample of synthetic fatty acids following the procedure described in Example 6. However, instead of the predominantly C_{13} synthetic fatty acids, the sample used contained proportions of C_{12} to C_{15}, wholly branched-chain, fatty acids prepared by a Koch-type reaction from a branched olefin which was itself prepared by co-dimerisation of linear hexenes with a C_6—C_8 α-olefin feedstock.

The lathering properties of the soap tablets were determined using the procedure described in Example 6, and were compared with the results obtained for two further soap tablets, one produced exclusively from the tallow fatty acids and the other from a mixture of tallow fatty acids and synthetic fatty acids in the proportions 50:50, which is outside the scope of the present invention. The results are shown in Table 5 below:

TABLE 5

Soap Description	Tallow fatty acids %	Synthetic (Branched-chain) fatty acids %	Lather Volume (Average results in mls) 20°C	40°C
Example 7	80	20	272	266
Comparative Soap	65	35	200	159
Comparative Soap	50	50	134	81
All Tallow Soap	100	0	175	184

These results demonstrate the beneficial lathering properties of the soap tablets prepared from proportions of branched-chain fatty acids within the range claimed.

In order to demonstrate the necessity for using branched-chain fatty acids having carbon chain lengths within the range stated in accordance with this invention, further soap tablets were prepared by the procedure described in Example 6 from a mixture of tallow fatty acids and synthetic fatty acids in the proportions of 75:25. The sample of synthetic fatty acids used contained predominantly α-methyl palmitic acid (C_{17}), so that the percentage of branched-chain fatty acids in the soap was therefore about 25%. The lathering properties of the tablet were determined by the procedure described above for Example 6 with the results given below.

Soap Description	Lather Volume (average results in mls) 20°C	40°C
Comparative soap (75:25 — tallow fatty acids: α-methyl palmitic acid)	138	141

These results show that the addition of the synthetic fatty acid of longer chain length than desired in accordance with the invention causes a deterioration in the lathering properties compared with the all tallow soap, rather than the improvement achieved in Example 7 using branched-chain fatty acids of chain length within the desired range.

EXAMPLE 8

A soap tablet was prepared from a mixture of tallow and synthetic fatty acids in the proportions 65:35 by addition of caustic soda solution (30% NaOH) to the heated mixed fatty acids in a crutcher mixer. The amount of caustic soda used was such that 10% of the total fatty acids were unneutralised. The resultant soap was cooled and air-dried at 60°C, following which small amounts of preservatives and titanium oxide were admixed with the dried soap which was milled and then extruded and pressed into soap tablets.

The sample of synthetic fatty acid used had the following approximate homologous distribution, C_{10} 3%, C_{11} 7%, C_{12} 28%, C_{13} 29%, C_{14} 22% and C_{15} 11%. About 75% of the fatty acids were linear fatty acids, the remainder being predominantly α-methyl branched-chain fatty acids.

The tablets so prepared, which contained about 8.5% of branched-chain fatty acids on the total fatty acids, were tested to determine their lathering properties which are given in Table 6 below. For purposes of comparison some further tablets were similarly prepared using palm kernel oil instead of the synthetic fatty acids and the lathering properties for this tablet are also shown in the Table.

TABLE 6

Soap Description	% Branched-chain fatty acids	Lather Volume (Average results in mls.) 20°C	40°C
Example 8	8.5	500	465
Comparative Soap Tablet	0	494	485

These results show the tablets according to the invention to have outstanding lathering properties, which are of the same order as those achieved using a high proportion of palm kernel oil fatty acids in a superfatted toilet soap tablet.

WHAT WE CLAIM IS:—

1. A soap derived from fatty acids comprising tallow fatty acids and synthetic fatty acids, which synthetic fatty acids include from 5 to 30 per cent by weight of C_{11}—C_{15} branched chain fatty acids, other than solely α-methyl tetradecanoic acid, the percentages being based on the total amount of fatty acids.

2. A soap according to claim 1 wherein at least 10 per cent by weight of the total amount of fatty acids are branched-chain fatty acids.

3. A soap according to claim 2 wherein about 20 per cent by weight of the total amount of fatty acids are branched-chain fatty acids.

4. A soap according to any of the preceding claims wherein the fatty acids include a major proportion of tallow fatty acids.

5. A soap according to any of the preceding claims wherein the synthetic fatty acids comprise at least 40 per cent by weight of branched-chain fatty acids.

6. A soap according to any of the preceding claims wherein the synthetic fatty acids are prepared by oxidation of fatty alcohols produced by the catalytic reaction of olefins with carbon monoxide and hydrogen.

7. A soap according to any of claims 1 to 5 wherein the synthetic fatty acids are substantially wholly branched-chain fatty acids.

8. A soap according to claim 7 wherein the synthetic fatty acids are prepared by the catalytic reaction of olefins with carbon monoxide and water.

9. A soap according to claim 1 and substantially as herein described with reference

to any of Examples 1 to 4 and 6 to 8.

10. A soap according to claim 1 substantially as herein described with reference to Example 5.

11. A tablet formed of a soap according to any of the preceding claims.

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